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Highly efficient synthesis of cyclic carbonates from epoxides catalyzed by salen aluminum complexes with built-in "CO_2 capture" capability under mild conditions

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A series of monometallic salen aluminum complexes were prepared by covalent linkage of the imidazolium-based ionic liquid moieties containing various polyether chains with the salen ligand at the two sides of the 5,5′-position. The salen aluminum complexes proved to be efficient and recyclable homogeneous catalysts towards the organic solvent-free synthesis of cyclic carbonates from epoxides and CO_2 in the absence of a co-catalyst. The catalysts presented excellent "CO_2 capture" capability due to the molecules containing polyether chains and the metal aluminum center, in which >90% yield of cyclic carbonate could be obtained under mild conditions. The catalysts can be easily recovered and six times reused without significant loss of activity and selectivity. Moreover, based on experimental and previous work, the "CO_2 capture and activation" cycloaddition reaction mechanisms by monometallic or bimetallic salen aluminum complexes were both proposed.

Introduction

Carbon dioxide is one of the greenhouse effect gases but it has been attracting much attention as an inexpensive, nontoxic, nonflammable, bio-renewable and highly abundant single carbon atom (C1 resource) building block for organic synthesis in recent years.[1] Many procedures have been developed towards the easy and economical chemical fixation of CO_2.[2] Among these, the synthesis of five-membered cyclic carbonates *via* the 100% atom-economical cycloaddition of epoxides with CO_2 is one of the most promising ways because cyclic carbonate products are widely used as aprotic high-boiling polar solvents, electrolytes for lithium-ion batteries, precursors of polymeric materials, and fine chemical intermediates.[3] Therefore, various catalytic systems, including alkali metal halides,[4] quaternary ammonium[5] or quaternary phosphonium salts,[6] ionic liquids,[7] metalloporphyrins[8] or metallosalen complexes,[9] have been developed to promote this transformation so far.

Based on our previous work towards the biomimetic dioxygen activation[10] and CO_2 fixation[8a] over metalloporphyrin catalysts, metal salen complexes as another kind of enzyme-like catalyst have drawn our attention due to their unique nature, such as easy synthesis procedures, modulating the steric and electronic properties conveniently by changing metal centers.[9b] Many different binary salen catalysts for the coupling reaction of CO_2 and epoxides have been reported, in which a co-catalyst is required for the ring opening of the epoxide. With respect to the binary salen catalyst systems, multi-functional metallosalen complexes presented higher catalytic activity and selectivity due to the two or three catalytic sites in one catalyst molecule. It is not only unnecessary to use a co-catalyst, but also easy to explore the mechanism and reuse the catalyst.[11] In general, on the basis of the motif towards activating epoxide and CO_2, a Lewis acid (metal center) and an anion X^- (nucleophile) are required to build this kind of catalyst. Fig. 1 shows a catalytic motif for the double activation of an epoxide with this type of compound.

Aluminum, as a nontoxic, readily available, environmental benign and earth-abundant metal, is a better choice, because

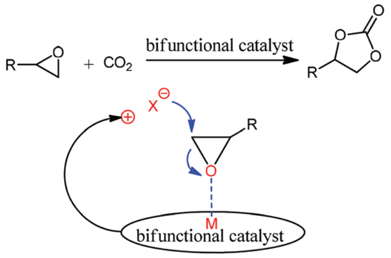

Fig. 1 Cooperative activation of epoxide with bi-functional catalyst.

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the stronger Lewis acidity is important for the ring-opening of the epoxide.[12] Most recently, a series of mononuclear bi-functional salen aluminum complexes containing quaternary ammonium salts[13] or quaternary phosphonium salts[14] tethered into the frame of the salen ligand in the context of organic cyclic carbonate formation under mild conditions have been reported. Even the μ-oxo-bimetallic salen aluminium complexes and their bi-functionalized compounds have been reported by North and co-workers, which provided a highly-active system under room temperature and atmospheric pressure conditions.[9d–g] However, in this case the introduction of highly polar ionic groups to these complexes often leads to the decreased solubility of catalyst in epoxide substrate; in turn, relatively low catalytic activity was obtained compared to the binary catalyst system. Meanwhile, distillation was necessary to recover the catalyst in each reaction cycle. Therefore, towards the fixation of CO_2 cyclic carbonates under mild conditions, the efficient and easy-recycling multifunctional salen catalyst is still desired.[15]

Polyethylene glycol (PEG) or polyethylene glycol monomethyl ether (*m*PEG), as an inexpensive, non-volatile and environmentally benign reagent, could be regarded as a CO_2-philic material through interaction of CO_2 with the oxygen atoms of the ether linkages of PEG or *m*PEG. More importantly, the "CO_2-expansion" effect could lead to changes in the physical properties of the liquid phase mixture including lowered viscosity and increased gas–liquid diffusion rates.[16] Addition of PEG or *m*PEG into the IL could enhance the rates of absorption of CO_2 significantly by decreasing the viscosity of the absorption system.[17] PEG-functionalized basic ionic liquids (ILs) have been proved to be highly efficient and stable catalysts for the cycloaddition reaction of CO_2 to epoxides.[18,19]

The "CO_2-expansion" effect of PEG or *m*PEG and the excellent reusability of the IL-functionalized salen complex[20] encourage us to prepare imidazolium IL containing polyethylene oxide (PEO) chain grafted salen aluminum complexes and catalyze the cycloaddition reaction of CO_2 with epoxide.[21] We envisage that the cooperative action of an anion X^- (nucleophile) and a metal center M (Lewis acid) of a catalyst promotes ring-opening of the epoxide, and polyether-based imidazolium IL units possess a built-in "CO_2 capture" capability.[22] The introduction of polyether chains can effectively solve CO_2 gas mass transfer in the liquid phase reaction system. Furthermore, the solubility properties of the PEG or *m*PEG with low molecular weight, that is, it is soluble in epoxide or product, but can be precipitated with ether, potentially endow the novel complexes with the feature of solvent-regulated separation.

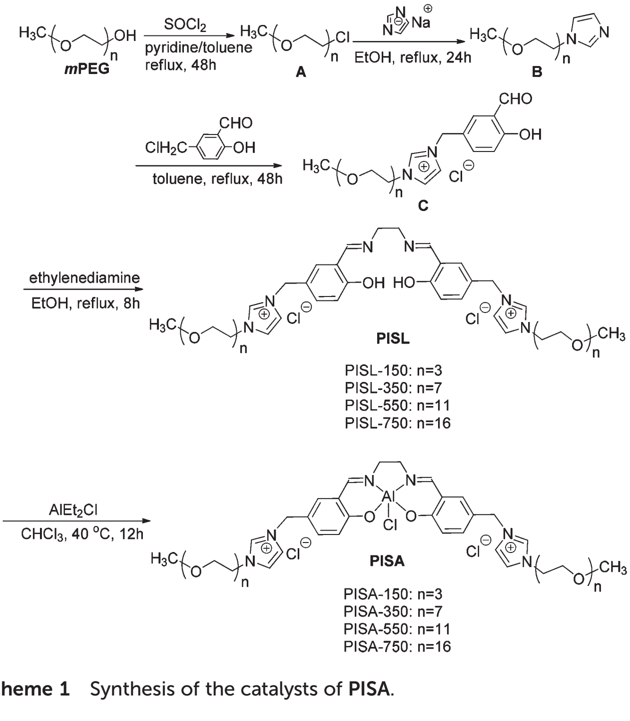
Herein, novel mononuclear salen aluminum complexes (denoted as PISA) were synthesized by covalent linkage of the imidazolium-IL moieties containing various PEO chains with the salen ligand at the two sides of 5,5′-position. It has been proved that these catalysts could embody an inherent "CO_2 capture" capability in the coupling reaction of CO_2 to epoxide under solvent-free and additive-free conditions. Thus, the enhanced solubility of the catalysts and the problem of gas–liquid phase mass transfer, even the separation of the catalysts, can be well resolved. Notably, these catalysts are easily recycled and can be conveniently reused, which is an important aspect in the development of practical coupling processes. In addition, it was found that the total length of the polyether chain in the range of low molecular weights has a certain influence on the catalytic performances of the novel complexes.

Results and discussion

Recently, chiral salen manganese complexes functionalized by polyether chain-modified imidazolium IL were first reported and acted as inherent phase-transfer catalysts in the enantioselective epoxidation of unfunctionalized olefins with aqueous NaOCl as an oxidant.[23] However, the long polyether chain prepared by auto-polymerization of explosive ethylene oxide possesses a broad molecular weight distribution and the hydroxyl at the end of the chain increased the uncertainty of the catalyst spatial structure. Therefore, polyether-based IL functionalized salen aluminum complexes were synthesized by a similar method using commercial *m*PEG with known molecular weight as the raw material. Meanwhile, the salen ligand was produced as the cheaper and readily-available salicyclaldehyde and ethylenediamine, which is beneficial for industrial production.

Preparation of PISA

The synthesis route for the **PISA** is outlined in Scheme 1. At first, *N*-(polyoxyethylene methyl ether) imidazole **B** with different numbers of polymerized ethylene oxide units (*n* = 7, 11, 16), was provided by combination between sodium



Scheme 1 Synthesis of the catalysts of **PISA**.

imidazole and chlorine-substituted *m*PEG **A**, and then **B** directly reacted with salicyclaldehyde to afford *m*PEG-based IL-substituted salicyclaldehyde **C**. The successive condensation between the aldehyde (–CHO) group of the compound C and the amino (–NH_2) groups of ethylenediamine was used to form the salen ligand **PISL**. Treatment of the **PISL** with diethyl aluminum chloride (0.9 M solution in toluene) under nitrogen gave the dianionic complex **PISA**. The newly-synthesized catalysts are light yellow solid powders at room temperature. Moreover, it is found that the **PISA** is miscible in some organic solvents, *e.g.*, ethanol, water and DMF, but can be precipitated with other organic solvents, *e.g.*, *n*-hexane, ether and ester. It is suggested that **PISA** should be an easily recoverable catalyst for the cycloaddition reaction by simple phase separation techniques *via* changing the solvents.

Catalytic performances

Firstly, the activity of various homogeneous monometallic catalysts such as **PISA-350** in the cycloaddition reaction of epoxides with CO_2 was explored using allyl glycidyl ether (AGE) as the model substrate under mild conditions in a semi-batch operation (CO_2 was continuously supplied to the reactor) and the results are shown in Table 1. To investigate the built-in stronger "CO_2 capture" capability originating from the PEO moiety, the traditional IL (1-benzyl-3-methylimidazoliumchloride, denoted as **IL**), the neat complex ([*N*,*N*′-bis(salicylidene)-ethylene diaminato] aluminum chloride, denoted as **SA**) and the simple IL-functionalized salen aluminum complex (denoted as **ISA1–4**) were also prepared for comparison (Chart 1).

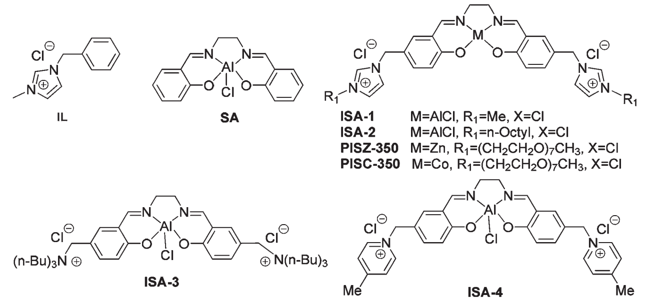
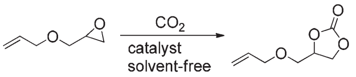


Chart 1 The structures of **IL**, **SA**, **ISA1-4**, **PISZ-350** and **PISC-350**.

Obviously, no reaction occurred when **SA** was used as the catalyst even after 24 h (Table 1, entry 1).[24] In addition, 0.5 mol% of the conventional **IL** could catalyze the cycloaddition reaction, but the yield of allyl glycidyl carbonate (AGC) was very low (Table 1, entry 2) under 1.0 MPa CO_2 pressure at 100 °C for 2.5 h under solvent-free conditions.[25] However, together with the equivalent mole ratio it represents an efficient binary catalyst system for the production of AGC (Table 1, entry 3). This observation encouraged us to evaluate the activity of various single component bi-functional catalysts in detail. As expected, catalyst **ISA-1** presented moderate yield in the absence of a co-catalyst in the coupling reaction of CO_2 to AGE (Table 1, entry 5). But it was less active than the catalyst **PISA-350** with 96% yield of AGC under the above conditions (Table 1, entry 9). It is worth noting that both of the catalysts presented excellent selectivity (>98%) towards cyclic carbonates. There is no other product such as polycarbonate as confirmed by FT-IR, ^1H NMR, ^{13}C NMR and GC-MS. The remarkable enhancement of reaction rates using catalyst

Table 1 Results of the cycloaddition reaction of AGE with CO_2 catalyzed by various catalysts[a]



Entry	Catalyst	*T*/°C	*p*(CO_2) /Mpa	Time/h	Conv.[b]/%	Yield[b]/%	TOF[c]/h^{-1}
1	**SA**	100	1	24	n.d.	n.d.	—
2	**IL**	100	1	2.5	16	15	12
3	**SA/IL (1 : 1)**	100	1	2.5	84	82	65.6
4	**PISL-350**	100	1	2.5	41	40	32
5	**ISA-1**	100	1	2.5	57	56	44.8
6	**ISA-2**	100	1	2.5	75	74	59.2
7	**ISA-3**	100	1	2.5	11	11	8.8
8	**ISA-4**	100	1	2.5	<3	2	1.6
9	**PISA-350**	100	1	2.5	96	95	76
10	**PISZ-350**	100	1	2.5	12	10	8
11	**PISC-350**	100	1	2.5	78	76	60.8
12	**PISA-350**	80	1	4	41	40	20
13	**PISA-350**	60	1	4	10	9	4.5
14	**PISA-350**	100	0.5	2.5	76	75	60
15	**PISA-350**	100	0.1	2.5	43	42	33.6
16	**ISA-1**	100	0.1	12	30	28	4.7
17	**PISA-350**	100	0.1	12	94	92	15.7
18	**PISA-350**	30	0.1	72	5	<3	<0.1

[a] Reaction conditions: 10 mL stainless-steel autoclave, AGE (6 mmol), catalyst (0.03 mmol). [b] Determined by GC using biphenyl as the internal standard. [c] Turnover frequency (TOF): mole of synthesized AGC per mole of catalyst per hour.

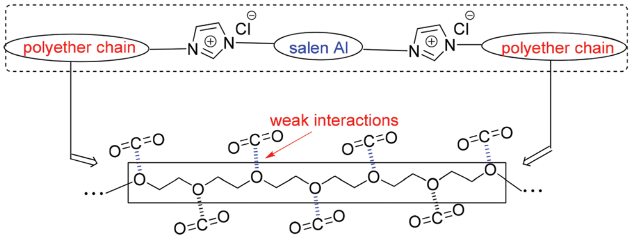


Fig. 2 Possible forms of "CO_2 capture".

PISA-350 under mild conditions could be attributed to the "CO_2-expansion" effect of PEO chains.[19,26] Since CO_2 is an electron acceptor and the oxyethylene (EO) group is an electron donor, the Lewis acid–base interaction between CO_2 and EO enhances the dissolution of CO_2 in the epoxide substrates (see Fig. 2). The weak interaction between electron-donating functional groups and CO_2 was detected by the *in situ* FT-IR technique reported by Kazarian and co-workers.[27] Moreover, a remarkable difference between **ISA-1** and **PISA-350** under 1 atm CO_2 pressure could also be observed. More than 92% yield of AGC with **PISA-350** as a catalyst was obtained at 100 °C after 12 h (Table 1, entry 17), whereas the catalyst **ISA-1** resulted in an extremely low yield (Table 1, entry 16).

In order to better understand the stronger "CO_2 capture" capability originating from polyether chains, we firstly investigated the catalytic activity of the simple IL-functionalized catalyst **ISA-2** with longer alkyl side chains without an oxygen atom on the imidazolium ring for comparison; when the length of the alkyl chain is increased from methyl to *n*-octyl group, the AGE conversion increased since the solubility of the catalyst in epoxide AGE increased with the increasing hydrophobic alkyl chain length (see Fig. 3). However, **ISA-2** exhibited lower activity with respect to **PISA-150** bearing three EO units with a similar hydrophobic alkyl chain length. This result suggests that the presence of the oxygen atoms within the PEO chains was crucial to the "CO_2 capture" capability of the catalyst, which is attributed to the weak interaction between the CO_2 molecule and the PEO chain. Moreover, bulky ILs, having longer distance between the cation and the anion, may be considered to have higher anion activation ability. Therefore, they are more effective in nucleophilic attack of the anion (X^-) to the epoxide ring of AGE due to the weak electrostatic interaction. It follows that the total length of the polyether chain in the range of low molecular weights directly affects the catalytic activity of catalysts in the coupling reactions.

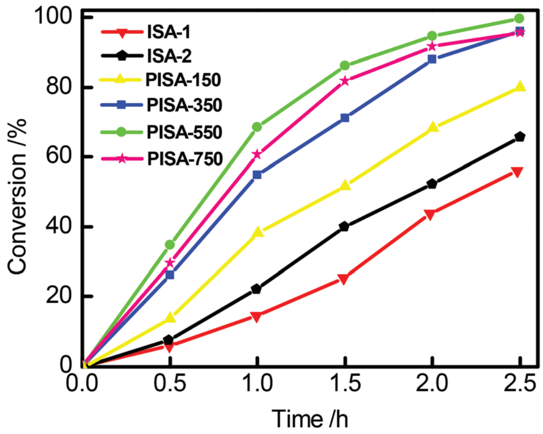


Fig. 3 Effect of reaction time on the catalytic performance of various catalysts. Reaction conditions: 10 mL stainless-steel autoclave, AGE (6 mmol), catalyst (0.03 mmol), CO_2 pressure (1.0 MPa), reaction temperature (100 °C).

Fig. 3 also shows the effect of reaction time on the catalytic performance of 0.5 mol% of the catalyst **PISA** with different lengths of polyether chain in the cycloaddition reaction of AGE with CO_2 at 1.0 MPa CO_2 pressure and 100 °C within 2.5 h. It clearly suggests that differences of reaction rates between various catalysts were observed. At relatively low pressure, the difference in solubility of CO_2 in PEG with different low molecular weights is negligible.[19] Thus, when the numbers of ethylene oxide units of the polyether chain increased from 3 to 11, appropriate increased yields of AGC were obtained, which indicated that the length of polyether chain within the catalyst has a certain effect on the coupling reaction. The **PISA-550** with eleven EO units presented the highest catalytic activity. However, when the EO numbers further increased to 16, a slightly decreased yield of AGC was observed. The subtle drop probably derives from the increased mass-transport limitation.[18a]

In consideration of a catalytic motif for the double activation of an epoxide in the coupling reaction system, it is found that the metal center, the imidazolium cation and halogen ions (X^-) were all important to obtain the high activity, which were indispensable. For instance, when directly using the IL-functionalized ligand **PISL-350** as a catalyst, it shows moderate activity (Table 1, entry 4) due to the lack of a metal center. Hence, the catalytic activity of a catalyst is closely related with the metal center; a substantial number of studies reported that catalysts containing a zinc ion or a cobalt ion were the most attractive for CO_2 coupling with epoxide owing to their high activity. However, the catalyst **PISZ-350** bearing a zinc cation has very low activity in cycloaddition reactions (Table 1, entry 10), which could be because Zn^{2+} owns weaker Lewis acidity than Al^{3+}.[8b] Additionally, using cobalt instead of aluminium as a metal center, the catalyst **PISC-350** exhibited higher activity with respect to the catalyst **PISZ-350** under identical conditions (Table 1, entry 11). Finally, it was noteworthy that the activities of **ISA-3** with quaternary ammonium-based ILs and **ISA-4** with pyridinium-based ILs were both obviously inferior to that of **ISA-1** (see Fig. 3), which shows that the incorporation of the imidazolium group within the salen ligand is beneficial for catalytic performance. It shows that both the metal center and the imidazolium cation are critical for the rate-determined step in the coupling reaction, which could activate and ring-open epoxides.

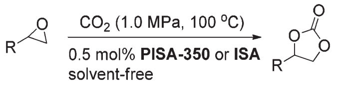
Furthermore, Table 1 also shows the effect of CO_2 pressure on the reactivity of **PISA-350** at 100 °C after 2.5 h. The conversion of AGE decreased as CO_2 pressure decreased from 1 to 0.5 MPa, further dropping to 0.1 MPa (Table 1, entries 14–15 *vs.* entry 9). Lower CO_2 pressure could reduce the absorption of CO_2 in the solution of AGE; in turn, the turnover frequency (TOF) was decreased.[28] In general, the cycloaddition reaction was more sensitive to temperature for other similar catalytic systems. While the reaction temperature dropped to 80 °C, and further dropped to 60 °C, the yield of AGC also decreased obviously (Table 1, entries 12–13 *vs.* entry 9). Unfortunately, the coupling reaction could basically not occur under room temperature and atmospheric pressure even for 72 h (Table 1, entry 18).

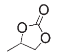
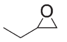
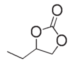
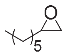
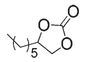
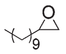
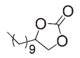
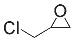
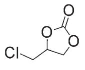
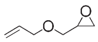
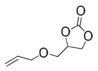
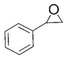
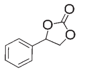
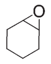
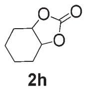
To evaluate the application range of the catalytic system, various epoxides, such as propylene oxide (PO), 1,2-epoxybutane, 1,2-epoxyoctane, 1,2-epoxydodecane, epichlorohydrin (ECH), styrene oxide (SO) and cyclohexene oxide (CHO), were used as the substrate for the reaction system using **PISA-350** as a catalyst. As shown in Table 2, most substrates could be smoothly converted to corresponding cyclic carbonates with high conversion and excellent selectivity (Table 2, entries 1–8). Both steric and electronic effects play an important role. The electron-withdrawing nature of the chloromethyl group of epichlorohydrin tends to drive the cycloaddition reaction for only 0.75 h under similar conditions (Table 2, entry 5).[15] Unfortunately, the internal epoxide, cyclohexene oxide, exhibited lower activity even after prolonging the reaction time to 24 h (Table 2, entry 8), presumably due to the high steric hindrance.[29] This steric effect was more likely to hinder the nucleophilic attack of the epoxide rather than its coordination to the Lewis acid metal center.[30] Especially, for 1,2-epoxyoctane and 1,2-epoxydodecane with a linear long alkyl chain (Table 2, entries 3–4), the excellent yields were obtained under quite mild conditions as a consequence of higher solubility of the catalyst **PISA-350** in epoxide substrate, while no activity was observed using the catalyst **ISA-1** under the same pressure and temperature due to the characteristics of insolubility. Therefore, catalysts **PISA** with PEO chains not only enhanced the activity but also improved the dissolution of the catalyst under solvent-free condition.

Recycling experiments

Based on the concept of "one-phase catalysis and two-phase separation"[20] and the special solubility of the **PISA**, the

Table 2 Results of the coupling reaction of CO_2 to various epoxide substrates over the **PISA-350** and **ISA-1**[a]



Entry	Epoxide	Product[b]	Time/h	Conv.[c] /%	Yield[c] /%	TOF[d]/h^{-1}
1	 **1a**	 **2a**	2	99 (50)	98 (49)	98 (49)
2	 **1b**	 **2b**	4	99 (37)	98 (36)	49 (18)
3	 **1c**	 **2c**	6	97 (0)	95 (0)	31.7 (0)
4	 **1d**	 **2d**	9	98 (0)	97 (0)	21.6 (0)
5	 **1e**	 **2e**	0.75	97 (74)	90 (68)	240 (181)
6	 **1f**	 **2f**	2.5	96 (57)	95 (56)	76 (44.8)
7	 **1g**	 **2g**	4	94 (33)	90 (31)	45 (15.5)
8	 **1h**	 **2h**	24	50 (24)	45 (22)	3.8 (1.8)

[a] Reaction conditions: 10 mL stainless-steel autoclave, epoxide (6 mmol), catalyst (0.03 mmol), CO_2 pressure (1.0 MPa), reaction temperature (100 °C), the value in parentheses refers to the catalyst **ISA-1**. [b] Product identification *via* FT-IR, ^{1}H NMR, ^{13}C NMR and GC-MS. [c] Same as in Table 1. [d] Same as in Table 1.

catalyst bearing PEO chains could be precipitated from the reaction solution by the addition of ether (Et_2O). The upper organic phase was obtained by simple decantation and the lower catalyst solid can be reused by adding fresh reaction substrates.

Experiments were also conducted to examine the recyclability and reusability of the **PISA-350** catalyst using AGE as the substrate under the optimal reaction conditions. The results indicate that the **PISA-350** catalyst could be reused for six successive runs without any significant loss in its catalytic activity, and the selectivity still remained at 98% (see Fig. 4), reflecting high stability of the catalyst. The comparative FT-IR analysis of the fresh catalyst **PISA-350**, **ISA-1**, **SA** and the recovered **PISA-350** after the 6th reuse in the cycloaddition reaction was performed, and the results are shown in Fig. 5. All the FT-IR spectra show characteristic vibration bands at around 1640 cm^{-1} and 1550 cm^{-1}, which are associated with the stretching vibration modes of C═N and C–O, respectively (Fig. 5a–d).[23] In addition, the stretching vibration ν(C–N) of the C–N bond in the IL units at around 1491 cm^{-1} and the stretching vibration of C–O–C groups in the PEO chain at 1098 cm^{-1} suggest the intact polyether-based imidazolium IL moiety on the salen ligand (Fig. 5b *vs.* 5a, 5c).[23]

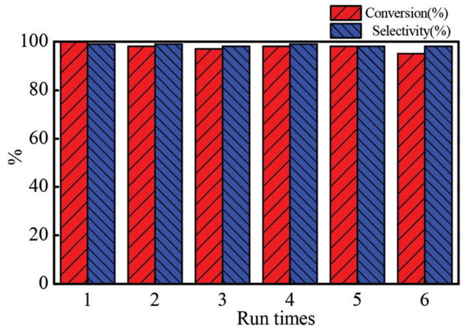


Fig. 4 Recyclability and reusability of the catalyst **PISA-350** in the coupling reaction of AEG with CO_2. Reaction conditions: 10 mL stainless-steel autoclave, AGE (6 mmol), catalyst (0.03 mmol), CO_2 pressure (1.0 MPa), reaction temperature (100 °C), reaction time: 3 h.

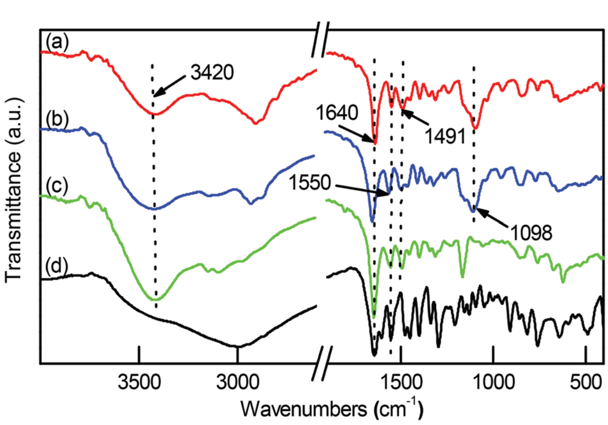


Fig. 5 FT-IR spectra of **PISA-350** (a), the recovered **PISA-350** after the 6th reuse in the cycloaddition reaction (b), **ISA-1** (c) and **SA** (d).

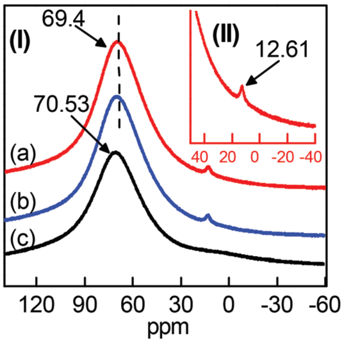


Fig. 6 (I) ^{27}Al NMR spectra of **PISA-350** (a), the recovered **PISA-350** (b) and **SA** (c); (II) ^{27}Al NMR spectra of **PISA-350** (partial amplification figure).

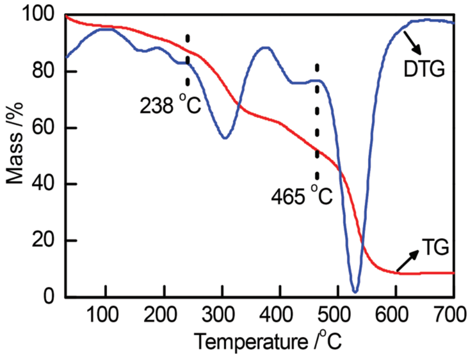


Fig. 7 Thermogravimetric (TG) and differential thermogravimetric (DTG) results of the catalyst **PISA-350**.

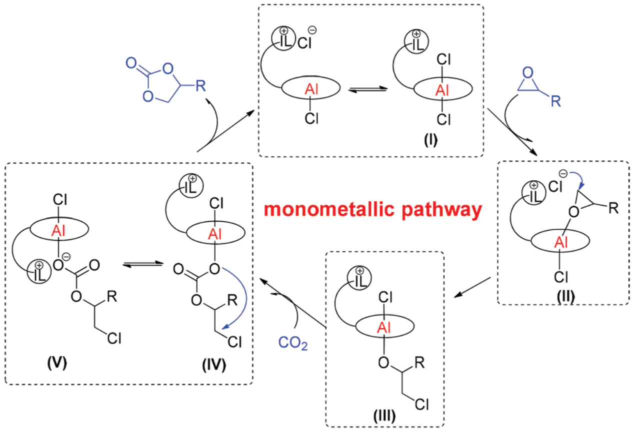
Moreover, ^{27}Al NMR spectra of complexes **SA**, **PISA-350** and the recovered catalyst **PISA-350** have all been found to display broad strong resonances around 70 ppm (Fig. 6a–c), which are usually attributed to five-coordinate aluminum species.[13] The results suggest that the recovered catalyst **PISA-350** presented here does not change the structure of catalytic active sites.

In addition, thermogravimetric analysis (TGA) results (see Fig. 7) proved that the **PISA-350** catalyst could endure about 238 °C with little loss of its weight. The decomposition of the ionic liquid started from about 465 °C, showing the high thermal stability.[20]

Reaction mechanism

Based on the molecular structure of the complex **PISA** and the cycloaddition reaction results, a possible mechanism[15] of the monometallic pathway involving two nucleophiles for cyclic carbonate synthesis was proposed, which is shown in Scheme 2.

At first, the anion of ionic liquid units in the catalyst **PISA** (Cl^-) coordinates to the metal in the remaining *trans* axial position, thus generating a six-coordinated intermediate (**I**).[13] As shown in Fig. 6, ^{27}Al NMR spectra of the complex **PISA-350** was found to display broad strong resonances at 69.4 ppm and a new weak signal around 12.61 ppm (see Fig. 6a), while the neat complex SA which lacks the attached imidazolium-based



Scheme 2 A plausible mechanism for the coupling reaction of epoxide with CO_2 catalyzed by **PISA** or **ISA-1**.

ionic liquid units on the salen ligand exhibits a single resonance at 70.53 ppm (see Fig. 6c). ^{27}Al resonance in complexes **PISA** or **ISA-1** is assigned to the five-coordinate aluminum species and the weaker and narrow up-field signal to a six-coordinate species. These observations were also reported by Liu and Darensbourg.[13,14] Subsequently, the coordination of the nucleophile (Cl^-) serves to labilize the other metal–chorine bond, favoring coordination and nucleophilic attack of the epoxide (**II**) activated by the metal center, followed by the ring opening. Meanwhile, the polyether-based IL units capture and activate the CO_2 molecule. Next, the formed alkoxide species (**III**) acts in turn as a nucleophile that attacks CO_2 to form a metal carbonate species (**IV**). Certainly, the imidazolium cations could also stabilize the metal alkoxide bond (**V**) through charge interactions. The subsequent ring-closure forms a relevant cyclic carbonate. In the meantime, the catalyst is regenerated. This mechanism insists that overall the role of the catalyst involves initial activation of the epoxide and stabilization of the ring-opened and carbonate intermediates formed during the reaction, which is important to reduce the reaction time and the pressure of the reaction.

Experimental

Reagents and methods

Polyethylene glycol monomethyl ether (*m*PEG, MW = 350, 550, 750) was purchased from Alfa Aesar Chemical Reagent Co. Ltd. Propylene oxide (PO), epichlorohydrin (ECH), allyl glycidyl ether (AGE), styrene oxide (SO), cyclohexene oxide (CHO), sodium ethoxide (*ca.* 21% in ethanol), tri-*n*-butylamine, 4-methylpyridine and diethyl aluminum chloride (Et_2AlCl, 0.9 M solution in toluene) were obtained by J&K Scientific Ltd. 1,2-Epoxybutane, 1,2-epoxyoctane and 1,2-epoxydodecane were used as received from TCI. Other commercially available chemicals were laboratory grade reagents from local suppliers. CO_2 was purified by passing through a column packed with 4A molecular sieves before use (99.99%). All of the solvents were purified by standard procedures.[31] 5-Chloromethylsalicylaldehyde was synthesized according to published procedures.[11a,32]

FT-IR spectra were obtained as potassium bromide pellets with a resolution of 4 cm^{-1} and 32 scans in the range 400–4000 cm^{-1} using a Bruker spectrophotometer. ^{1}H NMR, ^{13}C NMR and ^{27}Al NMR spectra were recorded on a Bruker Avance III 400 M spectrometer, using TMS, 1,4-dioxane and standard aqueous aluminum solution (1000 μg mL^{-1} certified atomic absorption standard solution) as a calibration reagent, respectively. The thermogravimetric and differential thermogravimetric (TG–DTG) curves were obtained on a NETZSCH STA 449C thermal analyzer. Samples were heated from room temperature up to 700 °C under flowing air using alumina sample holders. The sample weight was *ca.* 10 mg and the heating rate was 10 K min^{-1}. Thin layer chromatography (TLC) was conducted on glass plates coated with silica gel GF_{254}. The conversions and yields of cyclic carbonate products were measured by a GC2010 gas chromatograph (Shimadzu) equipped with the capillary column (Rtx-5, 30 m × 0.32 mm × 0.25 μm) and the FID detector.

Preparation of the polyether-based IL functionalized salen Al complex (PISA)

The preparation of **PISA** is outlined in Scheme 1.

Synthesis of chlorine-substituted poly(ethylene glycol)monomethyl ether (A).[33] To a 500 mL three-neck round bottom flask were added polyethylene glycol monomethyl ether (100 mmol, MW = 350, 550, 750), pyridine (15.82 g, 200 mmol) and dry toluene (200 mL) under a nitrogen atmosphere. The mixed solution was heated slowly to 80 °C and then thionyl chloride (23.79 g, 200 mmol) was added dropwise for 3 h. The mixture was stirred vigorously for an additional 48 h under reflux. After cooling to room temperature, a small amount of H_2O was added to quench the reaction, and the lower red salts were extracted with toluene three times, which merged into the upper organic phase. Afterwards, the pale-yellow organic phase concentrated and the residue was dissolved in CH_2Cl_2 (50 mL), washed with H_2O (3 × 50 mL), and then dried over anhydrous Na_2SO_4. The solvent was evaporated, dried *in vacuo* to give a pale-yellow liquid A. Yield: 90%. **A–350:** FT-IR (KBr), γ_{max}/cm^{-1}: 2874, 1457, 1353, 1300, 1250, 1200, 1112, 947, 851, 745, 664, 534; ^{1}H NMR ($CDCl_3$/TMS, 400 MHz), δ_H ppm: 3.67–3.70(t, 2H, J = 12 Hz, Cl–CH_2–CH_2), 3.55–3.60(m, 24H, $(OC_2H_4)_6$–O), 3.47–3.49(t, 2H, J = 8 Hz, Cl–CH_2–CH_2), 3.31(s, 3H, O–CH_3).

Synthesis of *N*-(polyoxyethylene methyl ether)imidazole (B).[34] *Ca.* 21% sodium ethoxide ethanol solution (16.2 g, 50 mmol) was added dropwise into the anhydrous ethanol solution (100 mL) of imidazole (3.4 g, 50 mmol) under stirring. The obtained mixture was refluxed for 8 h. After the completion of the reaction, chlorine-substituted poly(ethylene glycol) monomethyl ether **A** (50 mmol) was dissolved in anhydrous ethanol (50 mL) and added dropwise into the above solution; the resulting mixture was stirred under reflux for another 24 h before allowing to cool to room temperature. The residue was filtered and the filtrate was evaporated *in vacuo*, and then washed with Et_2O (3 × 20 mL) to give an orange-red viscous liquid **B**, used without further purification. Yield: 82%. **B–350**: FT-IR (KBr), γ_{max}/cm^{-1}: 3114, 2873, 1457, 1351, 1325, 1298, 1251, 1200, 1109, 950, 847, 753, 666, 618, 537; ^1H NMR ($CDCl_3$/TMS, 400 MHz), δ_H ppm: 7.62 (s, 1H, ring C*H*–N=C), 7.48 (s, 1H, ring N–C*H*=CH), 7.01(s, 1H, ring N–CH=C*H*), 4.02–4.05(t, 2H, *J* = 12 Hz, N–CH_2), 3.66–3.68(t, 2H, *J* = 8 Hz, N–CH_2CH_2), 3.52–3.58(m, 24H, $(OC_2H_4)_6$–O), 3.31(s, 3H, O–CH_3). ^{13}C NMR ($CDCl_3$/TMS, 100.4 MHz), δ_C ppm: 136.47, 128.00, 120.83, 70.89, 69.53, 69.47, 68.77, 65.60, 57.97, 46.06.

Synthesis of polyether-based IL modified salicycladehyde (C). *N*-(Polyoxyethylene methyl ether)imidazole **B** (30 mmol) in dry toluene (100 mL) was added dropwise into the stirring toluene solution of 5-chloromethylsalicylaldehyde (30 mmol, 5.1 g) under a nitrogen atmosphere. The reaction was heated to reflux for 48 h. After cooling, the solvent was evaporated *in vacuo* and the lower viscous liquid was washed three times with dry benzene (3 × 20 mL) and ether (3 × 50 mL), respectively. The solvent was removed to obtain compound **C** as the orange-red viscous liquids. Yield: 60%. **C-350**: FT-IR (KBr), γ_{max}/cm^{-1}: 3415, 3074, 2874, 1657, 1615, 1592, 1561, 1488, 1448, 1352, 1284, 1250, 1215, 1150, 1107, 931, 845, 770, 677, 632, 516, 458; ^1H NMR (D_2O, 400 MHz), δ_H ppm: 9.85(s, 1H, ring NC*H*), 9.75(s, 1H, C*H*=O), 8.65–8.89(s, 2H, ring NC*H*), 7.65(s, 1H, ring Ar*H*), 6.87–6.98(s, 2H, ring Ar*H*), 5.32(s, 2H, PhCH_2–N), 4.35–4.37(m, 2H, N–CH_2–CH_2), 3.83–3.85(m, 2H, N–CH_2–CH_2), 3.52–3.64(m, 24H, $(OC_2H_4)_6$–O), 3.31(s, 3H, O–CH_3). ^{13}C NMR (D_2O, 100.4 MHz), δ_C ppm: 196.39, 160.29, 137.43, 133.43, 125.54, 122.71, 122.25, 121.14, 118.16, 70.98, 69.65, 69.56, 69.43, 68.28, 58.05, 52.02, 51.91, 49.31.

Synthesis of the polyether-based IL functionalized salen ligand (PISL). The anhydrous ethanol solution (20 mL) of ethylenediamine (5 mmol, 0.3 g) was added dropwise into the solution of polyether-based ionic liquid modified salicylaldehyde **C** (10 mmol) in anhydrous ethanol (50 mL) in a 1 : 2 molar ratio at reflux. The resulting mixture was refluxed for another 8 h; following this, the solvent was evaporated to dryness and the polyether-based ionic liquid functionalized salen ligand **PISL** was obtained as a light yellow viscous liquid, used without further purification. Yield: 96%. **PISL-350**: FT-IR (KBr), γ_{max}/cm^{-1}: 3422, 2876, 1635, 1591, 1560, 1497, 1450, 1350, 1285, 1234, 1103, 943, 839, 759, 727, 667, 637, 518; ^1H NMR (D_2O, 400 MHz), δ_H ppm: 9.98(s, 2H, ring NC*H*), 8.41(s, 2H, C*H*=N), 7.89(s, 2H, ring NC*H*), 7.79(s, 2H, ring NC*H*), 7.00–7.20(m, 6H, ring Ar*H*), 5.10(s, 4H, Ph–CH_2–N_{ring}), 4.18–4.20(t, 4H, *J* = 8 Hz, N–CH_2–CH_2), 3.79–3.82(m, 4H, N–CH_2CH_2–N), 3.57–3.64(m, 48H, $(OC_2H_4)_6$–O), 3.32(s, 6H, O–CH_3).

Synthesis of PISA. Under nitrogen protection and constant stirring at 40 °C, to a 100 mL round-bottom flask containing the above-obtained salen ligand **D** (5 mmol), anhydrous chloroform (50 mL) was added *via* a hypodermic syringe to dissolve the ligand, and then a little excess of Et_2AlCl (0.9 M solution in toluene, 5.7 mL, 5.1 mmol) was added slowly. The reaction was highly exothermic and resulted in a yellow solution and a pale yellow solid. The resulting yellow mixture was refluxed for an additional 12 h. After removal of the solvent under vacuum, the mixture was washed with ether several times and then dried at 40 °C under vacuum to obtain light yellow powders of **PISA**. Yield: 90%. **For PISA-350**: FT-IR (KBr), γ_{max}/cm^{-1}: 3420, 3135, 2924, 1639, 1557, 1489, 1456, 1396, 1348, 1311, 1250, 1098, 949, 839, 761, 668, 641, 421; ^1H NMR (DMSO-d_6, 400 MHz), δ_H ppm: 9.41(s, 2H, ring NC*H*), 8.50(s, 2H, C*H*=N), 7.80–7.84(m, 4H, ring NC*H*), 7.42–7.59(m, 4H, ring Ar*H*), 6.87–6.89(m, 2H, ring Ar*H*), 5.37(s, 4H, Ph–CH_2–N_{ring}), 4.37–4.39(t, 4H, *J* = 8 Hz, N–CH_2–CH_2), 3.86–3.88(m, 4H, N–CH_2CH_2–N), 3.78–3.80(t, 4H, *J* = 8 Hz, N–CH_2–CH_2), 3.36–3.45(m, 48H, $(OC_2H_4)_6$–O), 3.32(s, 6H, O–CH_3); ^{13}C NMR (DMSO-d_6, 100.4 MHz), δ_C ppm: 168.50, 166.53, 138.85, 138.16, 135.16, 130.14, 124.99, 123.86, 123.33, 121.22, 73.11, 71.61, 69.92, 59.88, 54.93, 50.74, 38.41; ^{27}Al NMR (DMSO-d_6, 104.3 MHz), δ_{Al} ppm: 69.4, 12.61; **For PISA-550**: FT-IR (KBr), γ_{max}/cm^{-1}: 3421, 2909, 1636, 1549, 1496, 1397, 1346, 1282, 1233, 1088, 1033, 952, 832, 757, 665, 630, 418; ^1H NMR (DMSO-d_6, 400 MHz), δ_H ppm: 9.42(s, 2H, ring NC*H*), 8.49(s, 2H, C*H*=N), 7.80–7.85(s, 4H, ring NC*H*), 7.42–7.59(m, 4H, ring Ar*H*), 6.82–6.94(m, 2H, ring Ar*H*), 5.38(s, 4H, Ph–CH_2–N_{ring}), 4.38–4.39(t, 4H, N–CH_2–CH_2), 3.85–3.89(m, 4H, N–CH_2CH_2–N), 3.78–3.80(t, 4H, *J* = 8 Hz, N–CH_2–CH_2), 3.42–3.56(m, 80H, $(OC_2H_4)_6$–O), 3.23(s, 6H, O–CH_3); ^{13}C NMR (DMSO-d_6, 100.4 MHz), δ_C ppm: 168.65, 165.92, 138.92, 136.93, 136.65, 135.11, 130.46, 126.92, 123.33, 121.12, 73.12, 71.62, 71.42, 57.84, 54.88, 50.65, 39.23; ^{27}Al NMR (DMSO-d_6, 104.3 MHz), δ_{Al} ppm: 69.36, 12.50; **For PISA-750**: FT-IR (KBr), γ_{max}/cm^{-1}: 3408, 2870, 1639, 1549, 1492, 1448, 1395, 1349, 1310, 1250, 1098, 949, 839, 761, 635, 526, 492, 420; ^1H NMR (DMSO-d_6, 400 MHz), δ_H ppm: 8.95(s, 2H, ring NC*H*), 8.52(s, 2H, CH=N), 7.91–7.93(s, 4H, ring NC*H*), 7.39–7.58(m, 4H, ring Ar*H*), 6.86–6.92(m, 2H, ring Ar*H*), 5.43(s, 4H, Ph–CH_2–N_{ring}), 4.37–4.41(t, 4H, N–CH_2–CH_2), 3.91–3.95(m, 4H, N–CH_2CH_2–N), 3.76–3.85(t, 4H, N–CH_2–CH_2), 3.42–3.51(m, 120H, $(OC_2H_4)_6$–O), 3.23(s, 6H, O–CH_3); ^{13}C NMR (DMSO-d_6, 100.4 MHz), δ_C ppm: 167.21, 165.20, 136.86, 136.47, 134.49, 128.91, 123.61, 123.03, 122.50, 119.90, 71.75, 70.25, 70.18, 68.57, 58.52, 53.55, 51.79, 36.87; ^{27}Al NMR (DMSO-d_6, 104.3 MHz), δ_{Al} ppm: 69.28, 12.42.

Synthesis of 1-benzyl-3-methylimidazoliumchloride. A solution of benzyl chloride (0.1 mol, 12.68 g) in toluene (200 mL) was mixed with a solution of 4-methylpyridine (0.1 mmol, 9.3 g) and refluxed overnight. After cooling to room temperature, the yellow viscous liquids were collected under vacuum following washing with ether several times. ^1H NMR ($CDCl_3$/TMS, 400 MHz), δ_H ppm: 10.49 (s, 1H, ring NC*H*), 7.72(s, 1H, ring NC*H*), 7.56(s, 2H, ring NC*H*), 7.49–7.51(s, 2H, ring Ar*H*), 7.33–7.34(s, 3H, ring Ar*H*), 5.58(s, 2H, CH_2), 4.04(s, 3H, CH_3); ^{13}C NMR ($CDCl_3$/TMS, 400 MHz), δ_C ppm: 137.14, 133.30, 129.15, 129.13, 128.70, 123.82, 121.95, 57.24, 52.86, 36.36, 18.33.

Synthesis of the neat salen Al complex (SA).[24b] FT-IR (KBr), γ_{max}/cm^{-1}: 2987, 1641, 1605, 1550, 1474, 1453, 1400, 1340, 1297, 1242, 1206, 1153, 1129, 1094, 1052, 1033, 1004, 987, 957, 908, 858, 814, 759, 635, 592, 555, 486, 464; ^1H NMR (DMSO-d_6, 400 MHz), δ_H ppm: 8.53(s, 2H, C*H*=N), 7.35–7.41(s, 4H, ring

Ar*H*), 6.85–6.87(d, 2H, J = 8 Hz, ring Ar*H*), 6.71–6.75(t, 2H, J = 16 Hz, ring Ar*H*); ^{13}C NMR (DMSO-d_6, 100.4 MHz), δ_C ppm: 167.59, 164.96, 135.50, 134.60, 121.65, 120.05, 116.38, 53.53; ^{27}Al NMR (DMSO-d_6, 104.3 MHz), δ_{Al} ppm: 70.53.

Synthesis of the simple IL-functionalized salen Al complex (ISA1–4). Following a similar procedure to that for the above newly-synthesized complex (**PISA**), simple IL-functionalized salen Al complexes (denoted as **ISA1–4**) were also prepared using 1-methylimidazole 1-octylimidazole, tri-*n*-butylamine and 4-methylpyridine, instead of **B** respectively. **ISA-1**: FT-IR (KBr), $\gamma_{max/}$cm^{-1}: 3417, 3095, 1642, 1552, 1489, 1397, 1310, 1225, 1164, 1054, 853, 758, 671, 620; ^{1}H NMR (DMSO-d_6, 400 MHz), δ_H ppm: 9.40(s, 2H, ring NC*H*), 8.51(s, 2H, C*H*═N), 7.75–7.82(s, 4H, ring NC*H*), 7.47–7.53(s, 4H, ring Ar*H*), 6.88–6.90(s, 2H, ring Ar*H*), 5.36(s, 4H, Ph–C*H*$_2$–N$_{ring}$), 3.88(s, 6H, N–C*H*$_3$). 3.85–3.86 (m, 4H, N–C*H*$_2$C*H*$_2$–N); ^{13}C NMR (DMSO-d_6, 100.4 MHz), δ_C ppm: 167.19, 165.15, 137.07, 135.83, 128.67, 125.78, 124.38, 122.59, 119.72, 118.75, 53.55, 51.59, 36.33; ^{27}Al NMR (DMSO-d_6, 104.3 MHz), δ_{Al} ppm: 70.38, 12.61.

Cycloaddition procedure for the reaction of epoxides with CO$_2$. Epoxide (6 mmol), catalyst (0.03 mmol) and biphenyl (0.6 mmol, internal standard for GC analysis) were added into a 10 mL stainless-steel autoclave equipped with a magnetic stirrer, which had been previously dried at 100 °C for 2.5 h under vacuum. After the reaction mixture was rapidly heated to the desired temperature (100 °C), the autoclave was pressurized with CO$_2$ from a reservoir tank to maintain a constant pressure (1.0 MPa). After stirring at *ca.* 200 rpm for the designated reaction time, the autoclave was cooled quickly to −5 °C and the remaining CO$_2$ was slowly released and absorbed in a small amount of ethyl acetate or ether. Subsequently, 20 mL ether was added into the reactor, and the catalyst was separated as a solid by centrifugation, which was washed with Et$_2$O or EA three times and dried under vacuum for the recycling experiment without further purification. Each catalytic reaction was repeated three times to secure reproducibility. The purity and structure of products were also confirmed by FT-IR, ^{1}HNMR, ^{13}CNMR spectra and GC-MS (Shimadzu GCMS-QP2010) analysis.

NMR characterizations of the typical cyclic carbonate products were as follows: 4-methyl-1,3-dioxolan-2-one: ^{1}H NMR (CDCl$_3$/TMS, 400 MHz), δ_H ppm: 4.77–4.86 (m, 1H, ring C*H*–CH$_3$), 4.49–4.53 (t, 1H, J = 16 Hz, ring C*H*$_2$), 1.41–1.43 (d, 1H, J = 8 Hz, C*H*$_3$); ^{13}C NMR (CDCl$_3$, 100.4 MHz), δ_C ppm: 155.15 (*C*═O), 73.70 (ring *C*H–CH$_3$), 70.72 (ring *C*H$_2$), 19.31(*C*H$_3$); 4-hexyl-1,3-dioxolan-2-one: ^{1}H NMR (CDCl$_3$/TMS, 400 MHz), δ_H ppm: 4.68–4.75 (m, 1H, ring C*H*), 4.51–4.55 (t, 1H, J = 16 Hz, ring C*H*$_2$), 4.05–4.09 (t, 1H, J = 16 Hz, ring C*H*$_2$), 1.77–1.84 (m, 1H, C*H*$_2$CH$_2$CH), 1.64–1.72 (m, 1H, CH$_2$C*H*$_2$CH), 1.30–1.49 (m, 8H, CH$_3$ (C*H*$_2$)$_4$), 0.88–0.91 (t, 3H, J = 12 Hz, C*H*$_3$); ^{13}C NMR (CDCl$_3$, 100.4 MHz), δ_C ppm: 155.13(*C*═O), 77.10 (ring *C*H–CH$_2$), 69.43 (ring *C*H$_2$CH), 33.88 (*C*H$_2$CH$_2$), 31.51 (CH$_2$*C*H$_2$), 28.80 (*C*H$_2$CH$_2$), 24.33 (CH$_2$*C*H$_2$), 22.46 (CH$_2$*C*H$_2$), 19.31 (*C*H$_3$); 4-chloromethyl-1,3-dioxolan-2-one: ^{1}H NMR (CDCl$_3$/TMS, 400 MHz), δ_H ppm: 4.98–5.04 (m, 1H, *C*H–CH$_2$), 4.59–4.63 (t, 1H, ring C*H*$_2$), 4.40–4.44 (dd, 1H, ring C*H*$_2$), 3.80–3.84 (dd, 1H, C*H*$_2$–Cl), 3.72–3.76 (dd, 1H, C*H*$_2$–Cl); ^{13}C NMR (CDCl$_3$, 100.4 MHz), δ_C ppm: 154.35 (*C*═O), 74.38 (ring *C*H), 67.00 (ring *C*H$_2$), 43.86 (*C*H$_2$–Cl); 4-allyl-1,3-dioxolan-2-one: ^{1}H NMR (CDCl$_3$/TMS, 400 MHz), δ_H ppm: 5.83–5.94 (1H, CH$_2$═C*H*), 5.19–5.31 (2H, C*H*$_2$═CH), 4.84–4.87 (1H, ring CH$_2$═C*H*), 4.50–4.54 (1H, J = 16 Hz, ring C*H*$_2$–CH), 4.38–4.42 (1H, J = 16 Hz, ring C*H*$_2$–CH), 4.01–4.10 (2H, C*H*$_2$–CH═), 3.69–3.73 (1H, CH$_2$–C*H*), 3.60–3.64 (1H, C*H*$_2$–CH); ^{13}C NMR (CDCl$_3$, 100.4 MHz), δ_C ppm: 155.06 (*C*═O), 133.71 (*C*H$_2$═CH), 117.79 (*C*H$_2$═), 75.17 (*C*H$_2$–CH), 72.51 (ring *C*H), 68.86 (CH$_2$–*C*H═), 66.27 (ring *C*H$_2$); 4-phenyl-1,3-dioxolan-2-one: ^{1}H NMR (CDCl$_3$/TMS, 400 MHz), δ_H ppm: 7.28–7.38(m, 4H, ring Ar*H*), 5.58–5.62 (t, 1H, J = 16 Hz, PhC*H*O), 4.71–4.75 (t, 1H, J = 16 Hz, OC*H*$_2$), 4.26–4.30 (t, 1H, J = 16 Hz, OC*H*$_2$); ^{13}C NMR (CDCl$_3$, 100.4 MHz), δ_C ppm: 153.75 (*C*═O), 134.78 (Ph), 128.72 (Ph), 128.23 (Ph), 124.83 (Ph), 76.95 (Ph), 70.13 (*C*H$_2$).

Conclusions

Several salen Al complexes functionalized by polyether-based imidazolium ILs have been first prepared and act as catalysts for the cycloaddition reaction of CO$_2$ and various epoxides to provide cyclic carbonate under quite mild conditions. A remarkable enhancement of the reaction rates was observed over the one-component tri-functional catalysts at low CO$_2$ pressure due to the built-in "CO$_2$ capture" capability originating from the polyether chains. Among them, the catalyst of **PISA-550** showed the best catalytic activity, which afforded cyclic carbonate in good yield (90–98%) with high selectivity for various epoxides under mild conditions. Furthermore, the synthesis catalyst **PISA** could be facilely separated and recycled six times with only a slight loss in its catalytic activity by control of the solvent.

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